

FORM PTO-1390 TRADEMARK OFFICE (REV 9-2001)		U S DEPARTMENT OF COMMERCE PATENT AND	ATTORNEY'S DOCKET NUMBER
<b>TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371</b>		TS0858 US U S APPLICATION NO (If known, see 37 CFR 1.5)	
INTERNATIONAL APPLICATION NO. PCT/EP00/04997	INTERNATIONAL FILING DATE 30 May 2000	PRIORITY DATE CLAIMED 3 June 1999	
TITLE OF INVENTION: PROPENE RECOVERY			
APPLICANT(S) FOR DO/EO/US: GEUS, Eduard, Rudolf; HARRIS, John, William; and PEK, Johan, Jan, Barend			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<p>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.</p> <p>4. <input type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <ul style="list-style-type: none"> <li>a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ul> <p>6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <ul style="list-style-type: none"> <li>A <input type="checkbox"/> is attached hereto</li> <li>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</li> </ul> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <ul style="list-style-type: none"> <li>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input type="checkbox"/> have been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input checked="" type="checkbox"/> have not been made and will not be made.</li> </ul> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p>			
<b>Items 11 to 16 below concern document(s) or information included:</b>			
<p>11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</p> <p>14. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</p> <p>15. <input type="checkbox"/> A substitute specification.</p> <p>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825</p> <p>18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</p> <p>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</p> <p>20. <input checked="" type="checkbox"/> Other items or information: postcard for date stamping only</p>			

U41980059		INTERNATIONAL APPLICATION NO PCT/EP00/04997	ATTORNEY'S DOCKET NUMBER TS0858 US																
<p>21. <input checked="" type="checkbox"/> The following fees are submitted:</p> <p><b>Basic National Fee (37 CFR 1.492(a)(1)-(5)):</b></p> <p>Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... <b>\$104.00</b></p> <p>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... <b>\$890.00</b></p> <p>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$740.00</b></p> <p>International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$710.00</b></p> <p>International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) ..... <b>\$100.00</b></p>			CALCULATIONS PTO USE ONLY _____																
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>			<b>\$890.00</b>																
<p>Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th>CLAIMS</th> <th>NUMBER FILED</th> <th>NUMBER EXTRA</th> <th>RATE</th> </tr> </thead> <tbody> <tr> <td>Total Claims</td> <td>17 - 20 =</td> <td>0</td> <td>x \$ 18.00</td> </tr> <tr> <td>Independent Claims</td> <td>1 - 3 =</td> <td>0</td> <td>x \$ 84.00</td> </tr> <tr> <td>Multiple dependent claim(s) (if applicable)</td> <td></td> <td></td> <td>+ \$280.00</td> </tr> </tbody> </table>			CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	Total Claims	17 - 20 =	0	x \$ 18.00	Independent Claims	1 - 3 =	0	x \$ 84.00	Multiple dependent claim(s) (if applicable)			+ \$280.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE																
Total Claims	17 - 20 =	0	x \$ 18.00																
Independent Claims	1 - 3 =	0	x \$ 84.00																
Multiple dependent claim(s) (if applicable)			+ \$280.00																
<b>TOTAL OF ABOVE CALCULATIONS =</b>			<b>\$</b>																
<p><input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.</p>			<b>\$</b>																
<b>SUBTOTAL =</b>			<b>\$890.00</b>																
<p>Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).</p>			<b>\$</b>																
<b>TOTAL NATIONAL FEE =</b>			<b>\$</b>																
<p>Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property</p>			<b>+</b> <b>\$ 40.00</b>																
<b>TOTAL FEES ENCLOSED =</b>			<b>\$</b>																
			<b>Amount to be refunded:</b>																
			<b>charged:</b> <b>\$930.00</b>																
<p>a. <input type="checkbox"/> A check in the amount of \$ _____ cover the above fees is enclosed.</p> <p>b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>19-1800</u> in the amount of <u>\$ 930.00</u> to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>19-1800</u>. A duplicate copy of this sheet is enclosed.</p>																			
<p><b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</b></p>																			
<p>SEND ALL CORRESPONDENCE TO:</p> <p>Kimbley L. Muller SHELL OIL COMPANY INTELLECTUAL PROPERTY P. O. BOX 2463 HOUSTON, TX 77252-2463 713-241-2698 713-241-6617</p> <p><u>Kim Muller</u> SIGNATURE</p> <p><u>Kimbley L. Muller</u> NAME</p> <p><u>27,577</u> REGISTRATION NUMBER</p>																			

TS0858 US  
KLM:BAF

I hereby certify that this correspondence is being deposited with the United States Postal Service as Express Mail in an envelope addressed to Assistant Commissioner for Patents, Box PCT, Washington, D.C. 20231 on or before the date shown below.

5

*Barbara Fisher*Barbara Fisher  
Date: November 29, 2001

10

## THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PCT International Application of )  
GEUS, Eduard, Rudolf et al )  
15 Int. Appl No.: PCT/EP00/04997 )  
Int. Filing Date: 30 May 2000 )  
20 PROPENE RECOVERY ) 29 November 2001

ASSISTANT COMMISSIONER FOR PATENTS

25 Washington, DC 20231

PRELIMINARY AMENDMENT UNDER 37 CFR 1.115

30 Applicant request entry of the following amendments prior to consideration of the claims pending in the application.

## IN THE CLAIMS:

35 Amend claims: 2-7

2. (Amended) The process of claim 1, wherein the gaseous fraction obtained in the stripping section is supplied directly to the absorber section.

40 3. (Amended) The process of claim 1, wherein the higher boiling liquid fraction obtained in the absorber section is supplied to step (a).

4. (Amended) The process of claim 1, wherein the stripping section and the absorber section are combined in one distillation column.

5. (Amended) The process of claim 4, wherein the hydrocarbon rich liquid fraction obtained in step (a) is fed to a position in the distillation column above the feed inlet of the hydrocarbon rich gaseous fraction obtained in step (b).
6. (Amended) The process of claim 1, wherein the hydrogen separation selectivity of the membrane separation in step (b) is greater than 20, wherein the hydrogen separation selectivity is defined as the permeability ratio of hydrogen over methane. .
7. (Amended) The process of claim 1, wherein the methane separation selectivity of the membrane separation in step (b) is greater than 5, wherein the methane separation selectivity is defined as the permeability ratio of methane over propane.

Respectfully submitted,  
GEUS, Eduard, R., et al

Their Attorney: Kimbley L. Muller  
Reg. No.: 27,577  
Tele: (713)-241-2698  
Fax: (713)-241-6617

**MARKED UP VERSION OF AMENDED CLAIMS**

5

2. (Amended) The [P] process [according to] of claim 1, wherein the gaseous fraction obtained in the stripping section is supplied directly to the absorber section.

3. (Amended) The [P] process [according to any one] of claim[s] 1 [-2], wherein  
10 the higher boiling liquid fraction obtained in the absorber section is supplied to step (a).

4. (Amended) The [P] process [according to any one] of claim[s] 1 [-3], wherein  
the stripping section and the absorber section are combined in one distillation column.

15 5. (Amended) The [P] process [according to] of claim 4, wherein the hydrocarbon rich liquid fraction obtained in step (a) is fed to a position in the distillation column above the feed inlet of the hydrocarbon rich gaseous fraction obtained in step (b).

6. (Amended) The [P] process [according to any one] of claim[s] 1[-5], wherein  
20 the hydrogen separation selectivity of the membrane separation in step (b) is greater than 20, wherein the hydrogen separation selectivity is defined as the permeability ratio of hydrogen over methane. .

25 7. (Amended) The [P] process [according to any one] of claim[s] 1[-6], wherein  
the methane separation selectivity of the membrane separation in step (b) is greater than 5, wherein the methane separation selectivity is defined as the permeability ratio of methane over propane.

PROPENE RECOVERY

The invention is directed to a process to separate propene from the product stream obtained in a fluidized catalytic cracking process.

In a fluid catalytic cracking (FCC) process a mixture of hydrocarbons is prepared by means of catalytic cracking of a petroleum distillate or residue fraction. The hydrocarbon reactor effluent is separated in a separation section into gasoline, light and heavy cycle oil and gaseous products, for example methane, LPG, propene and butene. In a conventional separation section the reactor effluent is first separated in a so-called main fractionator. The top product obtained in the main fractionator will comprise next to the so-called permanent gases like hydrogen, methane and nitrogen a certain amount of ethene, ethane, propene, propane and other saturated and unsaturated hydrocarbon compounds having a boiling point of below 220 °C. The valuable hydrocarbon compounds boiling in the gasoline range are recovered from this top product in a so-called unsaturated gas plant as described in US-A-4605493.

US-A-4605493 describes a process in which the top product of the main fractionator is first compressed in one or more stages to a higher pressure level. This section is also referred to as the recontacting section. After the recontacting section the gaseous compounds having a boiling point of ethane and below are separated from the hydrocarbon products having a boiling point of at least propene and above by means of distillate separation step. This distillate separation step comprises in that the compressed top product is separated in a gaseous fraction and a liquid fraction by means of a

flash operation. The gaseous fraction is sent to an absorber section and the liquid product is sent to a stripping section. In the combined absorber and stripping section propene, propane and higher boiling hydrocarbon compounds are separated from the gaseous compounds including ethane and ethene and lower boiling compounds. In the embodiment illustrated in US-A-4605493 the absorber and stripping sections are represented by two separate vessels. Embodiments in which both sections are present in one column are also known from the prior art.

Propene has become an important by-product of a FCC unit operation. The importance of this by-product is for example illustrated by the fact that dedicated ZSM-5 containing catalyst additives are used to enhance the propene yield in a FCC unit operation. A problem often associated with the increase in propene yield above the design value of an existing plant is that the above described rectifying absorber becomes a bottleneck. This bottleneck may for example result in that the part of the extra propene prepared in the FCC reactor will not be separated from the gaseous products in the rectifying absorber. Recovery of propene from the gaseous product downstream of the rectifying absorber is economically less attractive.

The object of the present invention is to provide a process in which propene can be separated from the gaseous FCC products with a higher efficiency than is possible with prior art processes.

This object is achieved by the following process:  
Process to separate propene from gaseous fluid catalytic cracking products by performing the following steps:  
a) separating a feed mixture comprising the gaseous products, propene and other saturated and unsaturated hydrocarbons obtained in a fluid catalytic cracking

process into a hydrocarbon-rich liquid fraction and a hydrogen containing gaseous fraction,

- 5 b) separating the hydrogen containing gaseous fraction into a hydrogen-rich gaseous fraction and a hydrocarbon-rich gaseous fraction by means of a membrane separation,
- 10 c) supplying the hydrocarbon-rich gaseous fraction obtained in step (b) to an absorber section and obtaining in said absorber section a lower boiling fraction rich in gaseous products having a boiling point of ethane or below and supplying the hydrocarbon-rich liquid fraction obtained in step (a) to a stripper section and obtaining in said stripper section a higher boiling fraction comprising propene and hydrocarbons having a boiling point higher than ethane.

Applicants have found that by separating of part of the hydrogen present in the feed to the rectifying absorber in step (c) that the efficiency of the propene recovery is improved. This improvement enables one, for example, to either make use of smaller distillate units for new FCC units or to de-bottleneck existing FCC units enabling a higher propene production. An additional advantage is that hydrogen is obtained having a reasonable good quality in a relatively simple manner when compared to methods which can recover hydrogen from gaseous fractions at a point more down stream of the rectifying absorber. A further advantage is that in step (b) part of the sour gasses like H<sub>2</sub>S and HCN are removed with the hydrogen, thereby reducing the amount of corrosive compounds in step (c).

The feed mixture of step (a) is a mixture obtained in a FCC main fractionator comprising gaseous products and saturated and unsaturated hydrocarbons ranging from

CROSS-REFERENCE TO RELATED APPLICATION

methane to hydrocarbons having an atmospheric boiling point of about 250 °C and preferably to about 220 °C. Apart from hydrogen the gaseous FCC products comprise various components like NH<sub>3</sub>, H<sub>2</sub>S, CO, CO<sub>2</sub>, and H<sub>2</sub>O. The feed mixture has a pressure typically between 11 and 25 bars. The content of hydrogen in the hydrogen containing gaseous fraction will suitably be 3 vol.% or higher. In a typical FCC process the hydrogen content in the hydrogen containing gaseous fraction will be between 5-20 vol.%.

The separation in a liquid and gaseous fraction in step (a) can be achieved by a conventional flash operation, for example in a knock out vessel. It has been found advantageous to reduce the contaminant level (especially NH<sub>3</sub> and H<sub>2</sub>S) of the hydrogen containing gaseous fraction sent to step (b). This leads to a more hydrogen-rich gaseous fraction in step (b). Removal of sour gasses can be achieved by conventional methods. For example by contacting the feed prior to step (a) with water and separating in step (a) the feed mixture into a sour water fraction and the above mentioned hydrocarbon-rich liquid fraction and hydrogen containing gaseous fraction. Such a separation may be suitably performed in a three phase separation vessel.

Step (b) can be performed by making use of conventional membrane separation means, which are known to be selective of separating hydrogen from small hydrocarbons. Selective separation occurs when a pressure gradient across the membrane is applied. Preferably a hydrogen separation selectivity greater than 20, more preferably greater than 50, is required, wherein the selectivity is defined as the permeability ratio of hydrogen over methane. Permeability is defined as the

number of moles of a compound which permeates a membrane per square meters per day per bar of pressure difference.

It is also advantageous for the propene recovery in step (c) when membranes are used through which methane and ethane will permeate significantly faster than the heavier hydrocarbons (C<sub>3</sub>+). Preferably the membrane has a methane separation selectivity of greater than 5, wherein the selectivity is defined as the permeability ratio of methane over propane. Suitable membranes should further have a sufficient permeation rate for the hydrogen and should have a sufficient life time. Preferred membranes further show a good resistance to liquid hydrocarbons. The membranes can be made from either inorganic or organic material. Examples of inorganic materials are ceramic, carbon and molecular sieve materials. An example of a ceramic membrane is described in US-A-5827569. Organic membrane materials are preferably of a polymer material, for example polyaramid, polyetherimide and polyimid. Examples of commercial membrane systems which can be used in the process according to the invention are Medal of L'Air Liquide, Prism alpha of Air Products, Polysep of UOP and Membrane Systems (e.g. module B-H) of Ube.

The membrane is suitably in the form of a hollow fibre placed in a membrane unit in a conventional manner known to one skilled in the art. In such a membrane unit a bundle of hollow membrane fibres are placed in a vessel in such a manner that hydrogen present in the feed to the unit can pass the membrane fibre from the shell side to the inside of the fibre resulting in a second gaseous fraction rich in hydrogen and a gaseous fraction enriched in hydrocarbons. The vessel has outlet conduits and spaces to collect the hydrogen rich gaseous fraction collected in the fibres and inlet means at the shell side

DRAFTING ATTACHED

for the gaseous fraction and outlet means for the hydrocarbon rich fraction. In a preferred embodiment a number of such vessels are arranged in series in order to achieve the desired separation and to avoid the use of  
5 large vessels.

The temperature in step (b) is preferably at least 20 °C higher than the dew point of the hydrogen containing gaseous mixture send to step (b) when membrane materials are used which are sensitive to liquid  
10 hydrocarbons. Additional means for heating this gaseous mixture should then be provided to heat the hydrogen containing mixture prior to step (b). Preferably the temperature in step (b) is between 50-100 °C and more preferably between 70-90 °C.

The hydrogen containing gaseous fraction in step (b) suitably will have a pressure greater than 11 bar, preferably greater than 15 bar which enables an efficient separation in step (b). The pressure ratio of the pressure of the hydrogen containing gaseous mixture send to step (b) and the hydrogen-rich gaseous mixture obtained in step (b) is suitably greater than 2 and preferably greater than 5. Although the separation rate is negatively influenced when a low pressure ratio is used, it may in some cases be advantageous when the  
20 resulting higher pressure hydrogen-rich gaseous fraction is further purified. When the hydrogen-rich fraction is used as fuel higher pressure ratios may advantageously be applied. Preferably more than 50% of the hydrogen present in the hydrocarbon feed mixture is separated in step (b).  
25

In step (c) the hydrocarbon-rich gaseous fraction obtained in step (b) is supplied to an absorber section. This absorber section may be a single column or a combination of more columns which comprise at least means to condense the gaseous top product, means to recycle the  
30 condensed top product to the absorber section and means  
35

to discharge a higher boiling liquid fraction to the stripper section. This liquid fraction may be advantageously sent to step (a) in order to separate any gaseous compounds in this fraction before sending it to the stripper section. This latter embodiment is illustrated in US-A-4605493.

The absorber section may further be suitably provided with means to supply a liquid hydrocarbon mixture, which mixture is poor in at least propene, to the top or discharge end of the absorber section. This hydrocarbon mixture, also referred to as lean oil, serves to absorb into the liquid phase as much propene and other valuable higher boiling hydrocarbons in the absorber section before being discharged to the stripper section. Examples of suitable sources of lean oil are the higher boiling fraction obtained in a debutanizer or the condensed fraction directly obtained from the top product of the main fractionator of a fluidized catalytic cracking process. In the condenser the lower boiling gaseous fraction rich in gaseous products having a boiling point of ethane or below is obtained.

In step (c) the hydrocarbon-rich liquid fraction obtained in step (a) is supplied to a stripper section. The stripper section is provided with reboiler means to evaporate any lower boiling compounds resulting in a gaseous fraction, means to discharge the higher boiling fraction comprising propene and hydrocarbons having a boiling point higher than ethane and means to discharge the gaseous fraction to the absorber section. This gaseous fraction may be send to step (a) before being supplied to the absorber section as illustrated in US-A-4605493. However preferably the gaseous fraction obtained in the stripping section is send directly to the absorber section in order to achieve that the hydrogen concentration in the hydrogen containing gaseous fraction

obtained in step (a) is as high as possible. A higher hydrogen concentration is favourable for the efficiency of the membrane separation in step (b).

5 The stripper section may be a single column or a combination of more columns. An example of an embodiment of step (c) is described in the afore mentioned US-A-4605493. In a preferred embodiment absorber section and the stripping section are combined in one distillation column, optionally provided with one or more additional side-coolers and reboilers. Such a combined 10 column is referred to as a so-called rectifying absorber.

15 It has been found that the propene recovery is even further improved when the hydrocarbon-rich liquid fraction obtained in step (a) is fed to a position in the rectifying absorber column above the feed inlet of the hydrocarbon rich gaseous fraction obtained in step (b). Preferably between 2-6 practical trays are present 20 between these two inlets.

20 The operation conditions in the rectifying absorber may be those conventionally applied. The pressure at the top may typically range between 10 and 25 bars and the bottom temperature between 110 and 140 °C.

25 The higher boiling fraction comprising propene and hydrocarbons having a boiling point higher than ethene obtained in step (c) can be further processed in a conventional manner in which propene is recovered by distillation from the other hydrocarbon products.

30 The invention shall be illustrated making use of Figure 1A and Figure 1. Figure 1A represents a rectifying absorber column according to the state of the art. Via stream (1) a feed mixture comprising gaseous products, propene and other saturated and unsaturated hydrocarbons is supplied to a knock out vessel (2) resulting in a hydrocarbon-rich liquid fraction which is discharged via 35 stream (4) to the rectifying absorber column (5) and a

PCT/EP00/04997

hydrogen containing gaseous fraction which is discharged via stream (3) to the rectifying absorber column (5). The rectifying absorber column (5) is equipped with a gas outlet (8) for the gaseous top fraction, a condenser (9) and a condenser collection vessel (10) in which the gaseous components are separated via (11) from the condensed liquid fraction which liquid fraction is recycled via (12) to the top of the column. Via stream (13) lean oil is mixed with the gaseous top product up-stream of condenser (9). Most of the propene present in the gaseous fraction present in stream (8) will be absorbed by the lean oil and returned to the rectifying absorber via (12). The rectifying absorber is further equipped with a reboiler (7). Via stream (6) the liquid bottom fraction enriched in propene is discharged to downstream separation units.

Figure 1 represents a process according to the invention. The meaning of the reference signs is the same as in Figure 1A. In addition to the process represented in Figure 1A a membrane separation unit (14) is shown in which a hydrogen-rich gaseous fraction is obtained and discharged via (16) and a hydrocarbon-rich gaseous fraction is obtained which is supplied to the rectifying absorber column (5) via (15).

The invention is especially directed to a method for retrofitting an existing separation unit which is part of the down stream separation means of a fluid catalytic cracking unit, and wherein in the separation unit the gaseous compounds having a boiling point of ethane and below are separated from the hydrocarbon products having a boiling point of at least propene. The existing separation unit, which has also been described above, comprises an absorber and stripping sections and separation flash means in which the hydrocarbon feed is first separated in a liquid and gaseous fraction.

Preferably the absorber and stripping sections are combined in one rectifying absorber column. The retrofitting comprising adding means to remove hydrogen, preferably by means of membrane separation, from the gaseous fraction obtained in the flash separator.

5 Preferably use is made of existing feed inlets in the respective absorber and stripping sections for the gaseous fraction obtained in the membrane unit and the liquid fraction obtained in the flash separator.

10 The invention is also directed to the use of a membrane separator to remove hydrogen from a feed of a distillate separation unit which is used to separate gaseous compounds having a boiling point of ethane and below from hydrocarbon products having a boiling point of at least propene.

15 The invention will be illustrated by the following non-limiting examples which are calculations using a mathematical model describing the knock out vessel and the rectifying absorber. A conventional value for the membrane separation efficiency is used.

20 Example 1

25 To a knock out vessel a typical FCC compressed top product of the main fractionator is sent having a pressure of 17.1 bar. Hydrogen was separated from the gaseous mixture as obtained in the knock out vessel in a membrane separation unit resulting in a gaseous mixture rich in hydrocarbons. The hydrogen rich gaseous fraction obtained has a pressure of 2 bars. The hydrocarbon-rich mixture is supplied to a typical rectifying absorber at the same feed inlet location as the feed inlet location of the liquid fraction obtained in the knock out vessel. The propene recovery is 95.1% calculated on the feed mixture. See also Table 1.

Example 2

Example 1 is repeated except that the feed inlet of the gaseous mixture rich in hydrocarbons is 4 practical trays below the feed inlet of the liquid fraction obtained in the knock out vessel. The feed inlet position of the liquid fraction is the same as used in Example 1. The propene recovery is 96.1% calculated on the feed mixture. See also Table 1.

Example 3

Example 1 is repeated except that the membrane area is half of the area used in Example 1. The propene recovery is 93.3% calculated on the feed mixture. See also Table 1.

Example 4

Example 1 is repeated except that the membrane area is 50% larger than the area used in Example 1. The propene recovery is 95.8% calculated on the feed mixture. See also Table 1.

Comparative experiment A

Example 1 is repeated except that the mixture having the composition (I) is supplied directly to the rectifying absorber without making use the knock out vessel and the membrane unit. The location of the feed inlet is the same as in Example 1. The propene recovery is 89.2% calculated on the feed mixture.

Table 1

Example→	1	2	3	4
membrane area (M <sup>2</sup> )	6000	6000	3000	9000
Pressure of stream (11) (bar)	16.3	16.3	16.3	16.3
Fraction of H <sub>2</sub> removed (% on feed)	76	76	56	84
propene recovery (% on feed)	95.1	96.1	93.3	95.8
capacity increase compared to base case: Comparative experiment A	6%	11%	5%	9%

29. 05. 2001

ART 34 AMEND

(54)

TS 0858 PCTNEW SET OF CLAIMS

1. Process to separate propene from gaseous fluid catalytic cracking products by performing the following steps:

5 a) separating a feed mixture comprising the gaseous products, propene and other saturated and unsaturated hydrocarbons ranging from methane to hydrocarbons having a boiling point of 250 °C as obtained in a fluid catalytic cracking process into a hydrocarbon-rich liquid fraction and a hydrogen containing gaseous fraction,

10 b) separating the hydrogen containing gaseous fraction into a hydrogen-rich gaseous fraction and a hydrocarbon-rich gaseous fraction by means of a membrane separation at a temperature of between 50 and 100 °C,

15 c) supplying the hydrocarbon-rich gaseous fraction obtained in step (b) to an absorber section, wherein to the top or discharge end of the absorber section a liquid hydrocarbon mixture is supplied to, which hydrocarbon mixture is poor in propene, and obtaining in said absorber section a lower boiling fraction rich in gaseous

20 products having a boiling point of ethane or below and supplying the hydrocarbon-rich liquid fraction obtained in step (a) to a stripper section and obtaining in said stripper section a higher boiling fraction comprising propene and hydrocarbons having a boiling point higher

25 than ethane.

2. Process according to claim 1, wherein the gaseous fraction obtained in the stripping section is supplied directly to the absorber section.

## ART 34 AMDT

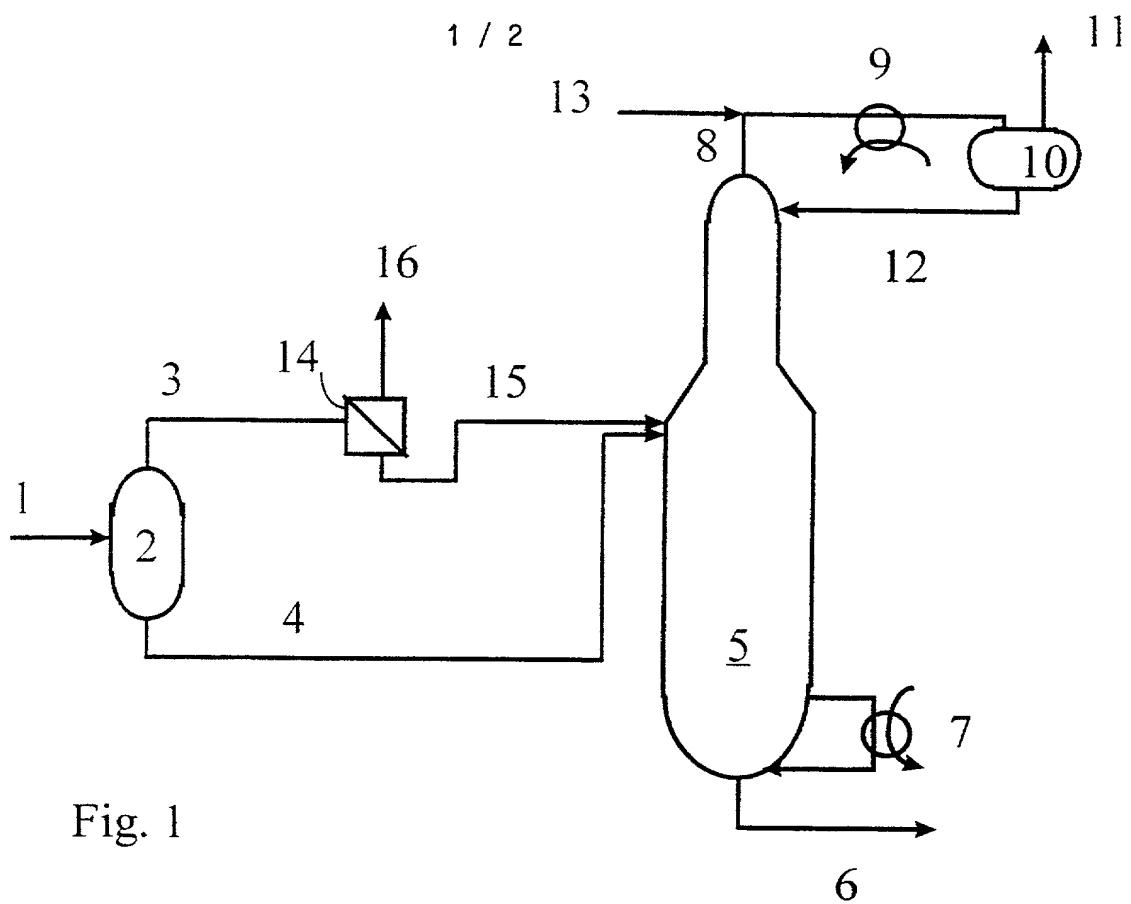
3. Process according to any one of claims 1-2, wherein the higher boiling liquid fraction obtained in the absorber section is supplied to step (a).

4. Process according to any one of claims 1-3, wherein  
5 the stripping section and the absorber section are combined in one distillation column.

5. Process according to claim 4, wherein the hydrocarbon rich liquid fraction obtained in step (a) is fed to a position in the distillation column above the feed inlet  
10 of the hydrocarbon rich gaseous fraction obtained in step (b).

6. Process according to any one of claims 1-5, wherein the hydrogen separation selectivity of the membrane separation in step (b) is greater than 20, wherein the hydrogen separation selectivity is defined as the  
15 permeability ratio of hydrogen over methane.

7. Process according to any one of claims 1-6, wherein the methane separation selectivity of the membrane separation in step (b) is greater than 5, wherein the methane separation selectivity is defined as the  
20 permeability ratio of methane over propane.



2 / 2

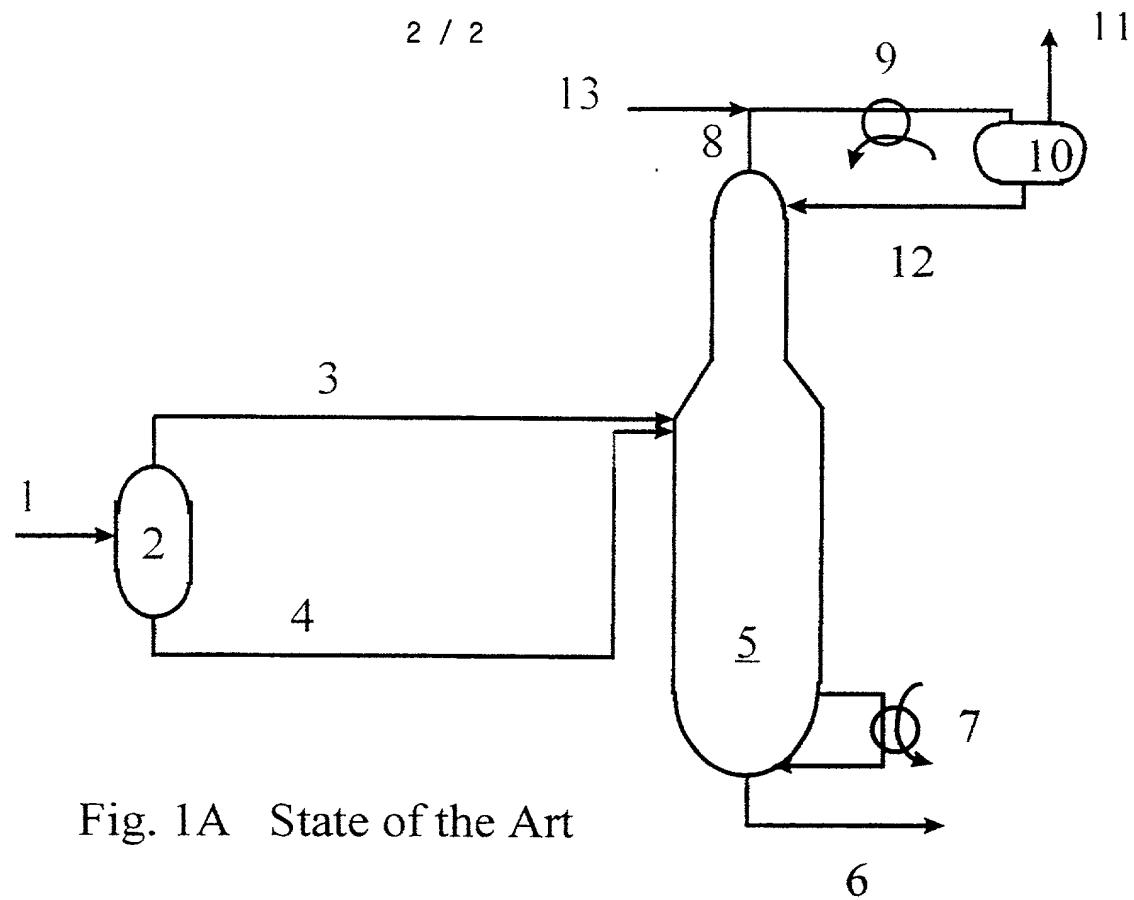


Fig. 1A State of the Art

# DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

ATTORNEY'S DOCKET NO. TS 0858 US A P
---

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

PROPENE RECOVERY

the specification of which is attached hereto

unless the following box is checked:

was filed on 30 MAY 2000 as United States Application Number or PCT International Application Number 99304349.6 and was amended on 29 MAY 2001 (if applicable).  
PCT/EP00/04997

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

PRIORITY FOREIGN APPLICATION(S)			Priority Not Claimed
APPLICATION NUMBER	COUNTRY	DAY/MONTH/YEAR FILED	
<u>99304349.6</u>	<u>EP</u>	<u>03 June 1999</u>	<input type="checkbox"/>
APPLICATION NUMBER	COUNTRY	DAY/MONTH/YEAR FILED	<input type="checkbox"/>

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below.

APPLICATION SERIAL NO.	FILING DATE

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s) or § 365(c) of any PCT International application designating the United States, listed below and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

APPLICATION SERIAL NO.	FILING DATE	STATUS-PATENTED, PENDING, ABANDONED

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

NAME <u>RICHARD F. LEMUTH</u>	ATTORNEY/AGENT <u>Attorney</u>	REGISTRATION NUMBER <u>30,081</u>	TELEPHONE NUMBER <u>(713) 241-3716</u>
NAME <u>Kimbley L. Muller</u>	ATTORNEY/AGENT <u>Attorney</u>	REGISTRATION NUMBER <u>27,577</u>	TELEPHONE NUMBER <u>(713) 241-2698</u>

Revised June 1995

## SEND CORRESPONDENCE TO:

(NAME) Richard F. Lemuth  
c/o Shell Oil Company  
Intellectual Property  
P.O. Box 2463  
Houston, TX 77252-2463

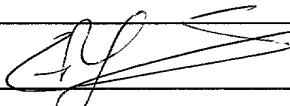
# DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

FULL NAME OF SOLE OR FIRST INVENTOR (given name, family name)

**GEUS, Eduard Rudolf**

INVENTOR'S SIGNATURE



DATE SIGNED

17 May 2000

RESIDENCE

**Badhuisweg 3, 1031 CM Amsterdam, the Netherlands**

**NLX**

CITIZENSHIP

**Netherlands**

POST OFFICE ADDRESS

**Badhuisweg 3, 1031 CM Amsterdam, the Netherlands**

FULL NAME OF SECOND JOINT INVENTOR, IF ANY (given name, family name)

**HARRIS, John William**

SECOND INVENTOR'S SIGNATURE



DATE SIGNED

17 May 2000

RESIDENCE

**Badhuisweg 3, 1031 CM Amsterdam, the Netherlands**

**NLX**

CITIZENSHIP

**Australian**

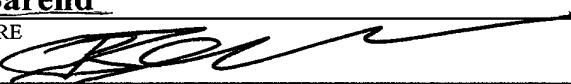
POST OFFICE ADDRESS

**Badhuisweg 3, 1031 CM Amsterdam, the Netherlands**

FULL NAME OF THIRD JOINT INVENTOR, IF ANY (given name, family name)

**PEK, Johan, Jan Barend**

THIRD INVENTOR'S SIGNATURE



DATE SIGNED

17 May 2000

RESIDENCE

**Badhuisweg 3, 1031 CM Amsterdam, the Netherlands**

**NLX**

CITIZENSHIP

**Netherlands**

POST OFFICE ADDRESS

**Badhuisweg 3, 1031 CM Amsterdam, the Netherlands**

FULL NAME OF FOURTH JOINT INVENTOR, IF ANY (given name, family name)

FOURTH INVENTOR'S SIGNATURE

DATE SIGNED

RESIDENCE

CITIZENSHIP

POST OFFICE ADDRESS

FULL NAME OF FIFTH JOINT INVENTOR, IF ANY (given name, family name)

FIFTH INVENTOR'S SIGNATURE

DATE SIGNED

RESIDENCE

CITIZENSHIP

POST OFFICE ADDRESS